



Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted Thiocalix[4]arenes

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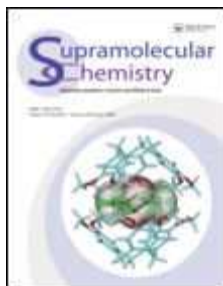
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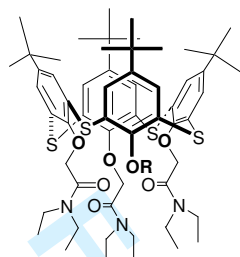
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**Synthesis and Complexation Properties Towards Metal Ions
of New Tri-substituted Thiacalix[4]arenes**

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Keywords:	thiacalix[4]arenes, synthesis, conformation, metal complexation



Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted Thiacalix[4]arenesS. Ben Maamar^{a,b}, N. Jadambaa^a, F. Vocanson^{a,c*}, F. Meganem^b, C. Felix^a, I. Bonnamour^a

TC1 R = H
TC2 R = nPropyl
TC3 R = Etylacetate

New thiacalix[4]arenes appended with three amide functions have been prepared. The complexation ability of these ligands towards various metal ions (Cd^{2+} , Pb^{2+} , Pd^{2+} ; Ni^{2+} , Hg^{2+} , Hg^+ , Ag^+ , Zn^{2+} and Cu^{2+}) has been investigated by UV-vis absorption.

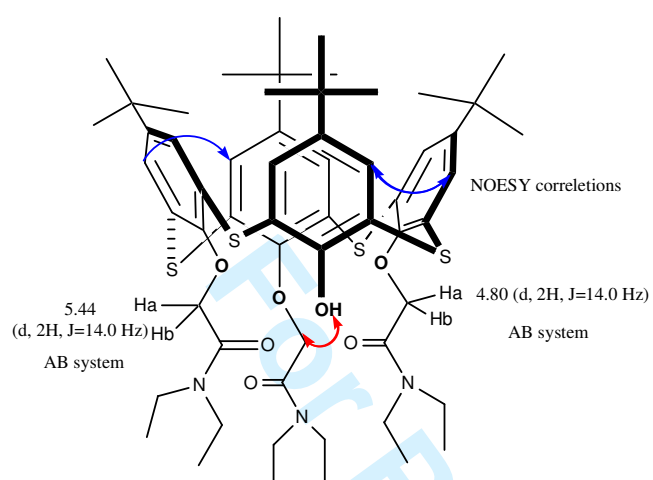


Figure 1. Conformational analysis of TC1.

CH_3CN resulting from additions of $\text{Pb}(\text{NO}_3)_2$ ($5 \cdot 10^{-4}$ M in acetonitrile/water, 3v/v).

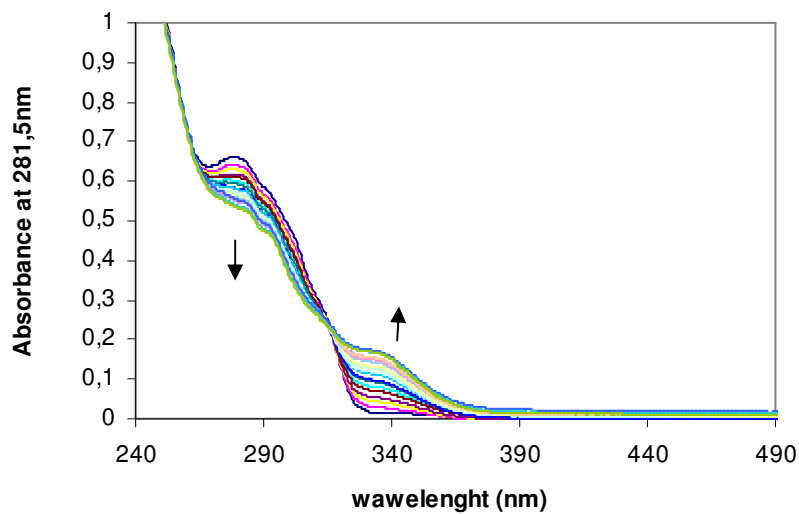
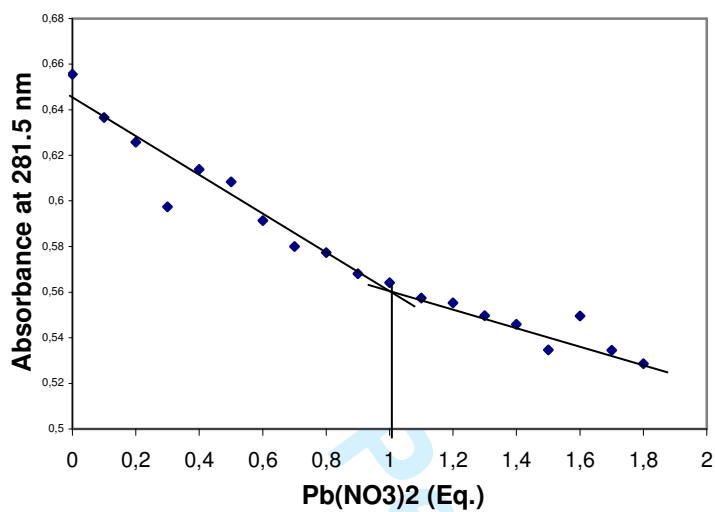
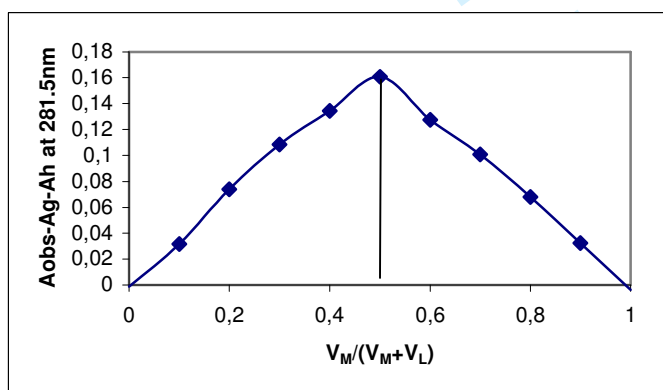


Figure 2. Changes in the absorbance spectrum of a 5.10^{-5} M solution of ligand **TC1** in CH_3CN resulting from additions of $\text{Pb}(\text{NO}_3)_2$ (5.10^{-4} M in acetonitrile/water, 3v/v).

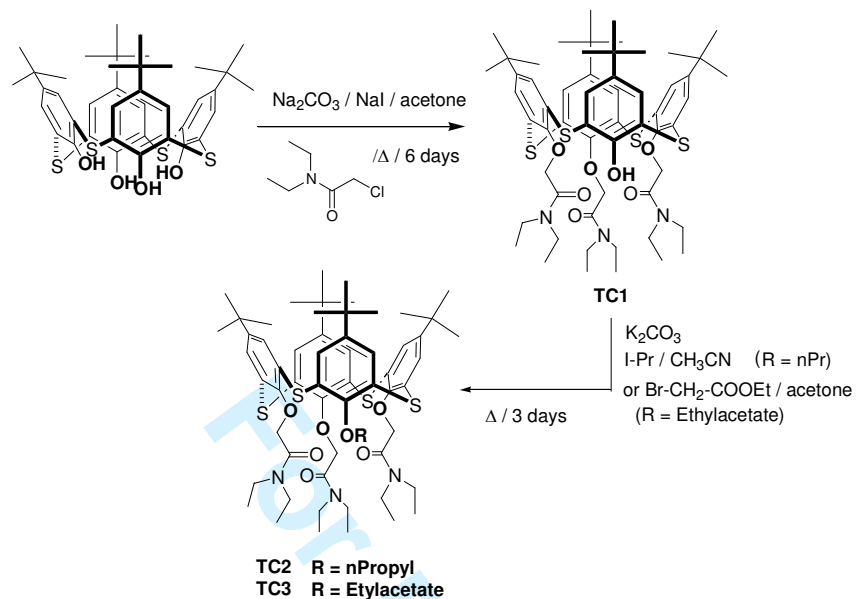


27 (a) Mole ratio method of Pb^{2+} -TC1 mixture



43 (b) Job plot of the titration of Pb^{2+} with TC1.

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46
47 Figure 3. Determination of the stoichiometry of Pb-ligand Complex



Scheme 1. Synthesis of triamide ligand derivatives.

*Supramolecular Chemistry***Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted
Thiacalix[4]arenes**

Abstract. New thiacalix[4]arenes appended with three amide functions have been prepared. Their conformations have been solved thanks to ^1H NMR 2D COSY and NOESY. The complexation ability of these ligands towards various metal ions (Cd^{2+} , Pb^{2+} , Pd^{2+} ; Ni^{2+} , Hg^{2+} , Hg^+ , Ag^+ , Zn^{2+} and Cu^{2+}) has been investigated by UV-vis absorption and the stoichiometry of the metal-ligand complexes was determined.

Keywords: thiacalix[4]arene, synthesis, conformation, metal complexation.

Introduction

Toxic heavy metals like copper, mercury, lead, nickel or cadmium can have a serious impact on the aqueous environment. So, detection and treatment of these toxic metal ions still remain an important topic. In this field, calixarenes, the well known cyclic oligomers of *p*-substituted phenols and formaldehyde, have attracted increased interest. Since the conventional

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2
3 calix[4]arenes have poor coordination ability towards metal ions, chemical modifications have
4
5 taken place by introducing functional groups having metal-binding ability. Recently, a new
6
7 class of macrocycles named thiacalixarenes has emerged. The presence of sulphur atoms
8
9 (which possess lone pairs and vacant 3d orbitals) instead of methylene bridges opens new
10
11 possibilities, especially in the field of metal complexation. The parent thiacalix[4]arene was
12
13 found to extract a wide range of transition metal ions from water, in contrast to classical
14
15 calix[4]arene (1). From many years, our group was interested in metal ions complexation and
16
17 extraction (2-4). Hence, we have previously reported the synthesis of a thiacalix[4]arene with
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19 tetra-amide functions at the lower rim (4). Extraction experiments have evidenced a remark-
20
21 able binding ability of this ligand towards a wide range of metal cations.
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27 With the aim of supplementing this study, we wondered about the role of the number of
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29 chelating groups. The lower rim functionalization of thiacalix[4]arene is becoming better
30
31 understood following the work of Lhotak (5,6) and Yamamoto (7). A few articles reports the
32
33 odd functionalisation of thiacalixarenes. Among them, for example the trimethylation of the
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35 hydroxyls of thiacalix[4]arene (5) was described (5) using K_2CO_3 in acetonitrile.
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39 In this paper, we describe the preparation of thiacalix[4]arenes substituted with tri-amide
40
41 functions at the lower rim. The complexation ability of these new ligands towards various
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43 metal ions has been investigated by UV-vis titration. The goal of this work is to dispose of a
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45 macrocycle which could be grafted on a surface without losing its complexation properties.
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50 51 **Preparation and characterization of the ligands**

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53 The synthetic route for the ligands **TC1-3** is depicted in Scheme 1. The O-alkylation of the
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55 lower rim of the parent *p-tert*-butylthiacalix[4]arene was achieved by action of Na_2CO_3 (3eq.)
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57 in acetone in presence of NaI, followed by 2-chloro-*N,N*-diethylacetamide. The reaction was
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59 refluxed three days and the crude product was purified by chromatography on silica gel to
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1
2
3 afford the pure **TC1**. ^1H and ^{13}C NMR spectra of **TC1** in CDCl_3 showed the presence of the
4 expected tri-amide derivative. However, it was difficult to determine the conformation of
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6
7
8 **TC1**. To complete the structural analysis, 2D COSY and NOESY experiments were
9
10 performed. The ^1H NMR shows two doublets and one singlet for the $\text{O-CH}_2\text{-C=O}$ signal. The
11
12 2D COSY confirms the presence of an AB system for two $\text{O-CH}_2\text{-C=O}$ groups and a singlet
13
14 for the third one (Figure 1). This AB system results from the rigidity of the calixarene
15
16 conformation and of the prochirality of two of the CH_2 groups. The 2D NOESY shows
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18 correlation spots between the aromatic hydrogens of neighboring phenyl moieties. A
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20 correlation spot is also present between one $\text{O-CH}_2\text{-C=O}$ group (corresponding to the singlet
21
22 signal) and the *OH* function (Figure 1). With the sight of these results, we can conclude that
23
24 the tri-substituted thiacalix[4]arene **TC1** adopts a cone conformation in solution. Then the
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26 derivatization of the thiacalixarene **TC1** was researched to establish the influence of the
27
28 substitution of the phenolic group on the complexation of metallic cations. At first **TC1** was
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30 alkylated with 1-iodopropane in refluxing acetonitrile in the presence of K_2CO_3 as a base. The
31
32 desired product **TC2** bearing three amide group and one propyl group was obtained after
33
34 chromatographic separation. **TC1** was also alkylated with ethylbromoacetate in refluxing
35
36 acetone in the presence of K_2CO_3 as a base. The desired product **TC3** bearing three amide
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38 group and one ethylacetate group was also obtained after chromatographic separation. The
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40 compounds **TC2** and **TC3** were identified by ^1H and ^{13}C NMR, and, ES-MS. The NMR
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42 analysis showed that the cone conformation was conserved for the two macrocyclic
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44 derivatives.
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55 **Complexation study**

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57 The UV-vis spectra of **TC1-3** show characteristic bands between 290 and 340 nm in CH_3CN /
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59 H_2O (3v/v). Complexation properties of **TC1-3** were studied towards various metal salts
60

(Cd²⁺, Pb²⁺, Pd²⁺, Ni²⁺, Hg²⁺, Hg⁺, Ag⁺, Zn²⁺ and Cu²⁺) by UV-vis titrations. In all cases, upon addition of metal cations solutions to a solution of **TC1-3**, spectra undergo clear changes and show the presence of isobestic points indicating the existence of complex species. The addition of aliquots of Pb²⁺ (from 0.2 to 1 equivalent) to a solution of **TC1** in a mixture of acetonitrile and water (3v/v) led to a decrease in the absorption bands at 280 nm and to the appearance of a new absorption band centred at 335.5 nm that is characteristic of a MLCT (Metal-Ligand Charge Transfer) band between Pb²⁺ and the nitrogen and oxygen atoms of the amide functions on the macrocycle (Figure 2). The isobestic point centred at 315.5 nm shows the formation of a new complex. Similar effects were observed upon addition of Ag⁺, Cd²⁺, Hg⁺, Zn²⁺, Pd²⁺ and Cu²⁺. Upon addition of cations solutions, we can observe in all cases a hypsochromic effect of the band at 285 nm and MLCT bands.

The stoichiometry of metal-ligand (M-L) complexes was determined both by the molar ratio (8) and the Job plot (9) methods (Figure 3). The results are given in Table 1. They indicate a 1:1 stoichiometry for five complexes (Ag⁺, Cd²⁺, Pb²⁺, Ni²⁺, Pd²⁺) in accordance with the literature data (10). We observed the formation of M_x-L_y complexes with Hg⁺, Cu²⁺ and Zn²⁺. It should be outlined that no complexation was observed for **TC1** with Hg²⁺. For comparison, the complexation of mercury salts by the tetra-amide-thiacalix[4]arene derivative was studied: this macrocycle does not retain Hg⁺ (11) ions but a complex is obtained between Hg²⁺ ions and the receptor in acetonitrile as solvent (5). Complexation properties of **TC2** are reported in Table 1. ML type complexes are obtained for Ag⁺, Zn²⁺, Pb²⁺, Ni²⁺ and Pd²⁺. Compared with the ligand **TC1**, we can highlight the formation of a monovalent complex with Zn²⁺. No complexation occurs with Hg⁺ whereas the addition of Hg²⁺ ions in a solution of **TC2** leads to the formation of a multivalent complex. The ligand **TC3**, bearing an ester group instead of a propyl chain, affords ML type complexes with Cd²⁺, Zn²⁺, Pb²⁺, Hg²⁺ and Pd²⁺. A ML₂ type complex is observed with Ag⁺.

The stability constants K are defined as the concentration ratio [Eq. (1)] :

$$(1) \quad K = \frac{[ML]}{[M][L]}$$

K can be correlated to the change in absorbance due to the formation of the ML complex.

Further modifications of the Benesi –Hildebrand method (12) result in an equation where a double reciprocal plot can be made with $1/\Delta A$ as a function of $1/[M]$ [Eq.(2)] :

$$(2) \quad \frac{1}{\Delta A} = \left[\frac{1}{\Delta \varepsilon [L]_0 K} \right] \left[\frac{1}{[M]} \right] + \frac{1}{\Delta \varepsilon [L]_0}$$

The logarithms of the stability constants (Log K) are collected in Table 2. Values of the stability constants seem to indicate that the cation Cd^{2+} is strongly complexed with ligand **TC1** undoubtedly because of its great affinity for N and O atoms. **TC2** and **TC3** ligands exhibit affinity in the same range for all metal cations. This indicates that the introduction of an ester function instead of a propyl chain does not affect their binding ability. These results also show that it will be possible to introduce on the ligand **TC1**, a spacer with a terminal function as silane or thiol allowing the grafting on a surface without loss of recognition. On this way **TC1** is more interesting than the thiacalixarene with the four tetra-amide functions.

Conclusion

New thiacalix[4]arene derivatives appended with three amide functions have been prepared and their conformation described. The complexation ability of these ligands towards various metal ions has been investigated by UV-vis absorption. These receptors exhibit similar

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2
3 complexation ability and selectivity except for Cd^{2+} . The main difference is observed for
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5 mercury salts. **TC1** binds selectively Hg^+ (*versus* Hg^{2+}), whereas **TC2** forms selectively a
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7 multivalent complex with Hg^{2+} (*versus* Hg^+) and **TC3** gives only a ML type complex with
8
9 Hg^{2+} . It seems that the number of amide groups doesn't play a crucial role (4), but the
10
11 presence of an OH function directs the selectivity towards the complexation of Hg^+ . The
12
13 extraction ability of **TC1** derivative for noble metals such as Pd^{2+} and Au^{3+} has been
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15 investigated by means of liquid-liquid extraction experiments (13). It has been observed that a
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17 similar behaviour is exhibited in the case of gold for the ligand **TC1** and for the
18
19 thiocalix[4]arene tetra-amide. In the case of palladium, the extraction efficiency increases
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21 with **TC1** ligand. Moreover, the new **TC1** derivative has been successfully used as carrier for
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23 Pd^{2+} and Au^{3+} transport in a SLM (supported liquid membrane).
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32 **Experimental section**

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34 **General methods.** Solvents were purified and dried by standard methods prior to use. All
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36 reactions were carried out under nitrogen. Column chromatography was performed with silica
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38 gel 60 (0.040-0.063 nm). Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were
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40 obtained at 300.13 and 75 MHz (CDCl_3 , TMS as internal standard, chemical shifts in ppm, J
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42 in Hertz). Mass spectra were obtained by electrospray technique (positive mode).
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48 **5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-*N,N*-diethylaminocarbonyl-28-hydroxythia-**

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50 **calix[4]arene **TC1**** (cone conformer). To a solution of 0.4g ($5.55 \cdot 10^{-4}$ mol) of *p*-*tert*-
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52 butylthiocalix[4]arene and 0.176g ($1.66 \cdot 10^{-3}$ mol) of Na_2CO_3 in acetone (60 mL), under
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54 nitrogen flux, was added 0.25g ($1.66 \cdot 10^{-3}$ mol) of NaI and 0.24 mL ($1.66 \cdot 10^{-3}$ mol) of 2-
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56 chloro-*N,N*-diethylacetamide. The mixture was refluxed for three days. The solvent was re-
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58 moved under vacuum. To the residue was added CHCl_3 (40 mL). The organic layer was sepa-
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60

rated, washed with water (2×20 mL) and dried over Na_2SO_4 . After removal of the solvent, the residue was purified by chromatography on silica gel (0.04-0.063 mm from Merck; eluted with heptane / CHCl_3 1:1) to afford pure **TC1** (286 mg, 48 %). ^1H NMR (300 MHz, CDCl_3) : $\delta = 9.18$ (s, H, Ar-OH), 7.53 (s, 2H, Ar-H), 7.38 (s, 2H, Ar-H), 7.12 (s, 4H, Ar-H), 5.54 (s, 2H, Ar-O- CH_2 -CO-), 5.44 (d, 2H (AB system), $^2J = 14.0$, Ar-O- CH_2 -CO-), 4.82 (d, 2H (AB system), $^2J = 14.0$, Ar-O- CH_2 -CO-), 3.51-3.34 (m, 12H, -CO-N(CH_2 - CH_3) $_2$), 1.32-0.94 (m, 54H, Ar-C(CH_3) $_3$, -CO-N(CH_2 - CH_3) $_2$). ^{13}C NMR (75 MHz, CDCl_3) : $\delta = 168.70$ and 167.72 (- CH_2 -CO-N-), 157.28 and 157.83 (ArC-O), 147.12, 145.57 et 142.03 (Ar-C(CH_3) $_3$), 135.53, 134.48 and 133.37 (ArC-H), 129.42 and 122.14 (ArC-S), 72.71 and 69.39 (Ar-O- CH_2 -CO-), 41.37 and 40.17 (-CO-N(CH_2 - CH_3) $_2$), 34.39 (Ar-C(CH_3) $_3$), 31.67 (Ar-C(CH_3) $_3$), 14.82 and 13.56 (CO-N(CH_2 - CH_3) $_2$). ES-MS. (positive mode) : mass (m/z) = 1060 $[\text{M}+\text{H}]^+$, 1082.4 $[\text{M}+\text{Na}]^+$. Mp = 138 °C.

5,11,17,23-tetra-*p*-tert-butyl-25,26,27-27-*N,N*-diethylaminocarbonyl-28-propyloxythiacalix[4]arene TC2 (cone conformer). To a solution of 0.1 g (0.094 mmol) of **TC1** and 0.065 g (0.471 mmol) of K_2CO_3 in acetonitrile (5 mL), under nitrogen flux, was added 0.092 mL (0.943 mmol) of 1-iodopropane. The mixture was refluxed for three days. The solvent was removed under vacuum. To the residue was added CHCl_3 (10 mL) and an aqueous solution of HCl 1N (10 mL). The organic layer was separated, washed with water (3×10 mL) and dried over Na_2SO_4 . After removal of the solvent, the residue was purified by chromatography on silica gel (0.04-0.063 mm from Merck; eluted with heptane / CHCl_3 60:40) to afford pure **TC2** (23 mg; 22 %) as white powder. ^1H NMR (300 MHz, CDCl_3) : $\delta = 7.43$ and 7.45 (d, 4H, Ar-H), 7.11 (s, 4H, Ar-H), 5.45 (s, 2H, O- CH_2 -CO-N(CH_2 - CH_3) $_2$), 5.04 (s, 4H, 2 -O- CH_2 -CO-N(CH_2 - CH_3) $_2$), 4.28 (t, 2H, $^3J = 7.72$, O- CH_2 - CH_2 - CH_3), 3.36-3.54 (m, 12H, 3 O- CH_2 -CO-N(CH_2 - CH_3) $_2$), 1.94-1.97 (m, 2H, O- CH_2 - CH_2 - CH_3), 1.04, 1.16 and 1.25 (m, 57 H, O-

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2
3 CH₂-CH₂-CH₃, 3 O-CH₂-CO-N(CH₂-CH₃)₂ and Ar-C(CH₃)₃). ¹³C NMR (75 MHz, CDCl₃) : δ
4
5 = 167.52 (Ar-O-CH₂-CO-), 158.01 (ArC-O), 146.92 (ArC-C(CH₃)₃), 134.85, 135.57 and
6
7 135.96 (ArC-H), 128.50, 129.17 and 130.96 (ArC-S-), 70.28 and 72.69 (Ar-O-CH₂-), 40.26,
8
9 41.56 and 41.78 (O-CH₂-CO-N(CH₂-CH₃)₂), 34.41 and 34.57 (Ar-C(CH₃)₃), 31.48, 31.67 and
10
11 31.83 (Ar-C(CH₃)₃), 24.23 (O-CH₂-CH₂-CH₃), 14.52 and 14.89 (O-CH₂-CO-N(CH₂-CH₃)₂),
12
13 13.44 (O-CH₂-CH₂-CH₃). ES-MS. (positive mode): mass (m/z) = 1102.5 [M+H]⁺, 1124.5
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15 [M+Na]⁺. Mp = 200 °C.
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22 **5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-*N,N*-diethylaminocarbonyl-28-ethoxycarbonylthia-**
23 **calix[4]arene TC3** (cone conformer). To a solution of 0.15 g (0.141 mmol) of **TC1** and 0.011
24
25 g (0.08 mmol) of K₂CO₃ in acetone (5 mL), under nitrogen flux, was added 0.031 mL (0.283
26
27 mmol) of ethylbromoacetate. The mixture was refluxed for three days. The solvent was
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29 removed under vacuum. To the residue was added CHCl₃ (20 mL) and an aqueous solution of
30
31 HCl 1N (10 mL). The organic layer was separated, washed with water (3 × 10 mL) and dried
32
33 over Na₂SO₄. After removal of the solvent, the residue was purified by chromatography on
34
35 silica gel (0.04-0.063 mm from Merck; eluted with heptane / CHCl₃ 60:40) to afford pure
36
37 **TC3** (81 mg; 50 %) as white powder. ¹H NMR (300 MHz, CDCl₃) : δ = 7.36, 7.52 and 7.64
38
39 (m, 6H, Ar-*H*), 7 (s, 2H, Ar-*H*), 4.73, 4.98 and 5.37 (m, 8H, 3 O-CH₂-CO-N(CH₂-CH₃)₂ and
40
41 O-CH₂-CO-O-CH₂-CH₃), 4.21 (q, 2H, ³J = 7.32, O-CH₂-CO-O-CH₂-CH₃), 3.21 and 3.41 (m,
42
43 12H, 3 O-CH₂-CO-N(CH₂-CH₃)₂), 1.10, 1.18, 1.25, 1.28 and 1.31 (m, 57H, 3 O-CH₂-CO-
44
45 N(CH₂-CH₃)₂, Ar-C(CH₃)₃ and O-CH₂-CO-O-CH₂-CH₃). ¹³C NMR (75 MHz, CDCl₃) : δ =
46
47 166.43 and 167.29 (Ar-O-CH₂-CO-), 156.03 and 158.44 (ArC-O), 149.82 (Ar-C(CH₃)₃),
48
49 136.80, 136.99 and 137.02 (ArC-H), 128.32, 130.43 and 130.94 (ArC-S-), 71.74 and 75 (Ar-
50
51 O-CH₂-), 61.74 (O-CH₂-CO-O-CH₂-CH₃), 40.44, 41.44 and 41.92 (O-CH₂-CO-N(CH₂-
52
53 CH₃)₂), 34.83 (Ar-C(CH₃)₃), 31.32 and 31.52 (Ar-C(CH₃)₃), 14.72 (O-CH₂-CO-O-CH₂-CH₃),
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2
3 13.40 and 14.57 (3 O-CH₂-CO-N(CH₂-CH₃)₂). ES-MS. (positive mode): mass (m/z) = 1146,4
4
5 [M+H]⁺, 1168,4 [M+Na]⁺. Mp = 215 °C.
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8
9

10 **Complexation.** The stability constants K defined as the concentration ratio [ML] / ([M][L])
11
12 (where M = cation and L = ligand) were determined at 18 °C, in acetonitrile or a mixture of
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14 acetonitrile/water (3v/v) by UV absorption spectrophotometry. The spectra were recorded on
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16 a Shimadzu UV-2401-PC. The procedure consisted in adding increasing amounts of metallic
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18 salts (5.10⁻⁴ M) to a solution of **PC1-3** ([**PC1-3**] = 5.10⁻⁵ M). The metal salts used were
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20 chlorides, perchlorates, nitrates or trifluoroacetates according to their solubility in the solvents
21
22 used. The following salts were used in pure acetonitrile : Cd(ClO₄)₂.H₂O, CF₃COOAg,
23
24 Zn(ClO₄)₂.6H₂O, Cu(ClO₄)₂.6H₂O, PdCl₂, (CF₃COO)₂Hg. In a mixture of acetonitrile/water
25
26 (3v/v) the following salts were used : Pb(NO₃)₂, NiCl₂.6H₂O, Hg(ClO₄)₂.4H₂O.
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Table 1. Stoichiometry of Metal-Ligand complexes.

	Cd ²⁺	Pd ²⁺	Pb ²⁺	Hg ⁺	Hg ²⁺	Zn ²⁺	Cu ²⁺	Ni ²⁺	Ag ⁺
TC1	ML	ML	ML	<i>a</i>	<i>b</i>	<i>a</i>	<i>a</i>	ML	ML
TC2	<i>a</i>	ML	ML	<i>b</i>	<i>a</i>	ML	<i>a</i>	ML	ML
TC3	ML	ML	ML	<i>b</i>	ML	ML	<i>a</i>	<i>a</i>	ML ₂

(a) M_x-L_y complexes are observed. (b) no complexation was observed.

Table 2. Stability constants of (1:1) Metal-Ligand complexes. LogK ($\lambda(\text{nm})$).

	Cd^{2+}	Pd^{2+}	Pb^{2+}	Hg^{2+}	Zn^{2+}	Ni^{2+}	Ag^+
TC1	8.04 (281.5)	2.69 (244.5)	4.51 (281.5)	-	-	4.42 (278)	4.14 (281)
TC2	-	3.21 (242.5)	4.76 (294.5)	-	4.28 (236)	4.07 (284)	3.78 (294)
TC3	4.20 (283)	3.21 (242.5)	2.82 (284.5)	4.61 (282.5)	2.28 (292)	-	-

It should be noted that these values are approximations of the ligand affinity. Indeed, error in our calculations due to the uncertainties involved in ϵ determination and concentration of the solutions cannot be neglected.